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THE RATE OF CRYSTALLIZATION OF CALCIUM SULFATE IN SULFITE LIQUOR IN THE PRESENCE OF SEEDING

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THE RATE OF CRYSTALLIZATION OF CALCIUM SULFATE IN SULFITE LIQUOR IN THE PRESENCE OF SEEDING [Skorost' Kristallizatsii Sul'fata Kal'tsiya v Sul'fitnom Shcheloke v Prisutstvii Zatravki]

by

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Sulfite liquor, obtained during boiling with acid and containing not only a calcium, but also a mixed calcium-sodium base, after preliminary concentration by evaporation is a supersaturated solution of calcium sulfate.

Independently of the degree of replacement of the calcium ion with a sodium ion in boiling acid during the two-step method used in industry involving the neutralization of the liquor by milk of lime and ammonia, the solubility curve of calcium sulfate passes through a minimum corresponding to a pH value of 3.5 for the liquor [1].

Upon introduction of a seeding of gypsum crystal into the calcium sulfite liquor, the supersaturation of the solution may be decreased to a significant degree [1, 2]. However, the rate at which the calcium sulfate solubility equilibrium state is attained in sulfite liquor is determined not only by the amount of seeding introduced,

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but also by a series of other factors, the important ones being: the temperature, and the amount of the original supersaturation of the solution before the introduction of active seeding.

The effect of the indicated parameters on the rate of crystallization of calcium sulfate was investigated for sulfite liquors of the Kotlasskiy (calcium base) and the Solikamskiy (calcium-sodium base) cellulose-paper combines. The liquors were concentrated by evaporation 1.3-1.5 times and neutralized by milk of lime to pH3.5. For purposes of comparison analogous experiments were carried out on purely aqueous solutions of calcium sulfate.

An active seeding of gypsum was introduced into the investigated solutions; the seeding was obtained by rapidly (1-2 sec) blending 76 percent sulphuric acid and milk of lime (80 g/l CaO) for 10-15 percent excess of the latter, and stirring the suspension at a rate of 1450 rpm [3]. The seeding was diluted with water to a crystalline gypsum content of 50 g/l.

As is apparent from Fig. 1 (a) the rate at which the equilibrium state is attained after the introduction of seeding into the calcium-sodium liquor increases with an increase in the seeding dose. With a tenfold increase in the amount of seeding (from 0.05 to 0.5 g/l) the time necessary for removal of supersaturation is divided by three. It is possible to significantly speed up this process by increasing the temperature of the liquor. Thus, if at a temperature of 70° C 90 min are required to attain the equilibrium state in this liquor, then at 90° C the required time is half as long (Fig. 1 [b]). Besides this, an increase in temperature promotes a more profound removal of the supersaturation of the solution; for example, at 70° C the calcium sulfate concentration at the equilibrium point is 2.19 g/l, and at 90° C it is lowered to 1.96 g/l, while during a change in the seeding dose within a wide range the calcium sulfate concentration at the equilibrium point remains constant.

Taking into account the fact that under industrial conditions significant fluctuations in the degree of supersaturation of sulfite liquor are possible, due to the regime of boiling, extraction, processing of the liquor, and others, a special investigation was made of the effect of this factor. To increase the supersaturation, calculated amounts of normal solutions of calcium chloride and sodium sulfate were introduced into the lye of the Solikamskiy combine. From Fig. 1 (c) it is apparent that the higher the degree of supersaturation, the more rapidly the equilibrium state is attained. However, the degree of supersaturation as well as the seeding dose do not affect the absolute value of the solubility at the equilibrium point.

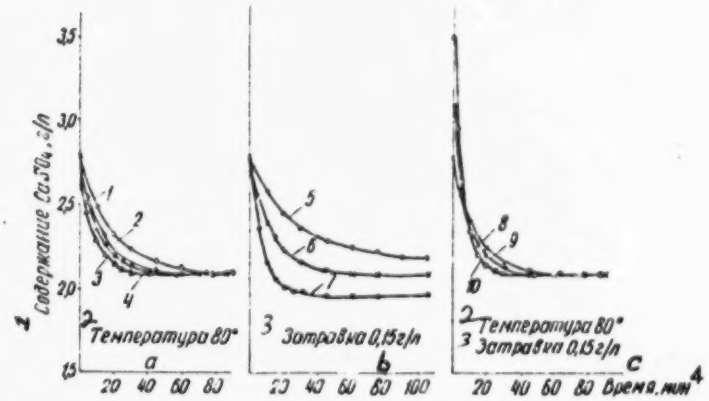

Fig. 1

Kinetic curves of removal of supersaturation by calcium sulfate of neutralized sulfite liquor based on a calcium-sodium mixture (pH 3.5) with: a - addition of seeding, g/l (1-0.05; 2-0.15; 3-0.25; 4-0.50); b - temperature, degrees C (5-70; 6-80; 7-90); c - original supersaturation, g/l (8-0.7; 9-1.0; 10-1.4)

Key:
1. $CaSO_4$ content, g/l
2. Temperature 80°
3. Seeding 0.15 g/l
4. Time, min

The overall character of the investigated dependences is most clearly traced if they are expressed in the form of crystallization rate constants. The constants were calculated using an equation describing a first-order reaction which (as I. I. Korol'kov and coworkers showed [4]) is obeyed by this process:

$$\ln\frac{C_0 - C_p}{C_\tau - C_p} = K\tau, \qquad C_p \equiv C_e$$

where C_0 is the original calcium sulfate concentration;

C_e is the equilibrium calcium sulfate concentration;

C_τ is the concentration at moment of time τ; and

K is the crystallization rate constant, min^{-1}.

Upon studying the effect of each factor on the calcium sulfate crystallization rate constant, a definite sequence in the position and character of the curves was detected (Fig. 2). Thus, the greatest value of the constants is observed for the purely aqueous calcium sulfate solution, followed by the curve for calcium lye; the smallest value of the constants is characteristic for the calcium-sodium lye.

Here it turned out that the crystallization rate constant increased most intensively upon the introduction of gypsum seeding from 0.05 to 0.25 g/l; upon further increase in the seeding concentration, the growth of the constant is slower.

When the temperature is increased an opposite dependence is found: the higher the temperature, the faster the crystallization rate constant grows in each solution. With an increase in the degree of the original supersaturation of the solution, this constant increases practically linearly; moreover, for all the solutions studied the tangent of the angle of inclination of the curves is constant.

The effect of the stirring intensity on the value of the crystallization rate constant was also studied. As is apparent from Fig. 2(d), in a wide range of number of revolutions of the mixer (from 150 to 1450) this effect is not noticeable. However,

here it is necessary to take into account the fact that in laboratory experiments during mixing at a rate less than 150 rpm, growing calcium sulfate crystals were already not maintained in a suspension state.

Thus, results of the studies show that the process of removal of supersaturation of sulfite liquor by dissolved calcium sulfate is completely regular, independent of the nature of the cations present in the liquor.

During development of regimes of crystallization under specific conditions of each cellulose-paper combine it is necessary, besides this, to take into account the different viscosities of the lyes, and also the presence in them of a complex of surface-active agents able to change the stability of the system and the rate of crystal growth (extractives, cymene, products of the vital activity of yeast, oligosaccharides, etc.).

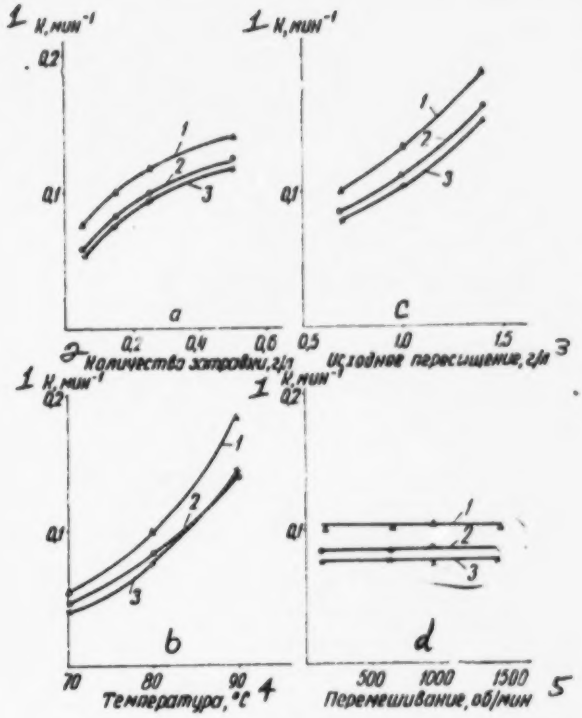

Fig. 2

Dependence of the crystallization rate constant for calcium sulfate in water and sulfite liquor on the effect of several factors (a - seeding dose; b - temperature; c - original supersaturation; d - mixing rate); 1 - calcium sulfate solution in water; 2 - calcium lye, pH 3.5; 3 - calcium-sodium lye, pH 3.5

Key:
1. K, min^{-1}
2. Amount of seeding, g/l
3. Original supersaturation, g/l
4. Temperature, ^{o} C
5. Mixing, rpm

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